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Polyhedral Oligomeric Silsesquioxane (POSS) cages $[RSiO_{1.5}]_n$ are a class of nano-particles that are being exploited as property modifiers to virtually every type of polymer imaginable. The most common of these materials are the $R_8Si_8O_{12}$ derivatives (also known as the T_8's), as the octomeric cage is preferentially formed in almost all synthetic pathways reported. However, well-defined oligomeric cages with n = 6, 10, 12 or 14 are also known and their polyhedral structures proven with single crystal X-ray crystallography.

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THERMODYNAMIC STABILITY AND KINETIC LABILITY OF FULLY-CONDENSED FLUORINATED POLYHEDRAL OLIGOMERIC SILSESQUIOXANE (POSS) CAGES

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Introduction

Polyhedral Oligomeric Silsesquioxane (POSS) cages [RSiO$_{1.5}$]$_n$ are a class of nano-particles that are being exploited as property modifiers to virtually every type of polymer imaginable.[1] The most common of these materials are the R$_8$Si$_8$O$_{12}$ derivatives (also known as the T$_8$'s), as the octomeric cage is preferentially formed in almost all synthetic pathways reported. However, well-defined oligomeric cages with n = 6, 10, 12 or 14 are also known[2] and their polyhedral structures proven with single crystal X-ray crystallography.[3] Representations of the unknown T$_4$ along with the most common POSS motifs are shown in Figure 1; for ease of viewing, a polyhedron made from just the silicon atoms is shown below each oligomer.
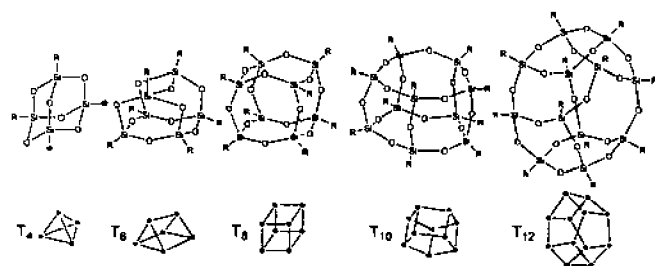

Figure 1. Representations of various [RSiO$_{1.5}$]$_n$ cages including the unknown T$_4$ along with the four most common oligomers, T$_6$, T$_8$, T$_{10}$ and T$_{12}$.

It was reported that under aggressive refluxing conditions with large relative quantities of sodium salts or base that some alkyl-substituted T$_8$'s can be converted to mixtures of mostly T$_8$, T$_{10}$ and T$_{12}$.[4] Theoretical calculations have also shown a higher enthalpic stability for the larger cages.[5] For this particular work, theoretical calculations on the relative enthalpies for these derivatives as a function of "R" group (methyl versus trifluoromethyl) were carried out along with laboratory experiments designed to measure the proportions of each cage under mild conditions conducive to isomerization.

Experimental

Materials. All POSS compounds were obtained from Hybrid Plastics or else synthesized according to the literature procedures.[6] NEt$_3$ was dried by refluxing over CaH$_2$ and distilled under dry nitrogen. CDCl$_3$ was first dried over CaH$_2$, then over molecular sieves, and vacuum transferred to a flask and stored under dry nitrogen. C$_6$F$_6$, AK225G (CClFH-CF$_2$-CF$_2$Cl) and Freon 113 (CCl$_2$F-CF$_2$Cl) were degassed prior to use.

Theoretical Calculations. The POSS cage geometries were optimized using density functional theory (DFT) methods.[7] The B3LYP hybrid functional[8], which included the SVWN5[9] correlation functional, was used in conjunction with the 6-311G(d,p)[10] basis set. All structures were verified as local minima via diagonalization of the matrix of energy second derivatives with respect to nuclear Cartesian coordinates (i.e., the hessian matrix.) Relative energies were refined by calculating single-point MP2[11] energies at the DFT geometries. All calculations were performed using the GAMESS[12] ab initio electronic structure code.

Results and Discussion

Calculations to determine the relative stabilities of a series of POSS cages, [RSiO$_{1.5}$]$_n$ with R = methyl or trifluoromethyl and n = 4, 6, 8, 10, 12, were undertaken to help understand the why some cage sizes appear to be preferentially formed. The data is shown in figure 2, along with correlating data from reference 5. Based on these numbers alone, one would expect that for enthalpic reasons (ΔH), larger cages would lead to a lower free energy of formation than smaller cages. However, the effect of entropy is not accounted for and entropy will always favor smaller cages (more particles). Another

factor that can play a role is a difference in solubility of various polyhedra. If during synthesis, one cage has a limited solubility in the reaction medium, it may preferentially precipitate and lead to high yield of a single isomer. Thus both thermodynamic and kinetic factors can be important.

ΔH	T$_4$	T$_6$	T$_8$	T$_{10}$	T$_{12}$
R = CH$_3$	0	-6.7	-7.8	-8.1	-8.1
R = CH$_3$	0	-6.7	-7.8	-	-
R = CF$_3$	0	-8.8	-11.2	-11.8	-12.3

Figure 2. Relative energy per silicon atom (kcal/mol) for the (CH$_3$)$_n$T$_n$ and (CF$_3$)$_n$T$_n$ series. The data in the top row is taken from reference 5b.

During the high-yield synthesis of various fluoroPOSS derivatives, [RSiO$_{1.5}$], R = CH$_2$CH$_2$(CF$_2$)$_m$CF$_3$, a variation in POSS cages was observed. When m = 3, 5, 7 or 9, then immediately after synthesis, cage mixtures were sometimes observed, but after a work-up procedure removed all traces of strong base (hydroxide), the isolated product was pure T$_8$ with, at most, traces of T$_{10}$ contaminant. The lone exception was the trifluoropropyl derivative (m = 0) which always yielded a cage mixture of T$_8$, T$_{10}$ and T$_{12}$.

When the pure T$_8$ compounds are dissolved in C$_6$F$_6$ and a fractional amount of a soft base such as NEt$_3$ is added, then the solution slowly changes over a period of days to a thermodynamic mixture of T$_8$, T$_{10}$, and T$_{12}$ along with traces of unidentified compounds that are presumably the higher oligomers. Interestingly, the proportion of the cages is the same for fluoropropyl, fluorohexyl and fluorooctylPOSS (m = 0, 3 or 5).
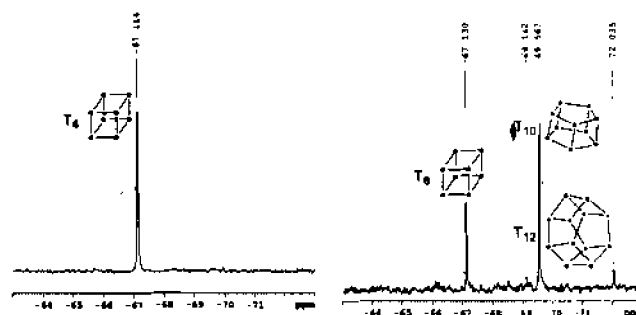

Figure 3. ^{29}Si NMR spectra of fluoropropyl$_x$T$_8$ in C$_6$F$_6$. On the left is a spectrum taken after 24 hours in solution without any added base. Shown on the right is the resulting mixture after 3 days with NEt$_3$.

The cages are completely stable in C$_6$F$_6$ solution without the addition of any base. Once triethylamine is added, it takes 2 - 3 days at room temperature to achieve what appears to be a thermodynamic equilibrium of which the molar proportions of T$_8$, T$_{10}$ and T$_{12}$ are about 40:50:10. Figure 3 shows this data along with the ^{29}Si assignments: the T$_8$ has 8 equivalent silicons resonating at -67.1 ppm; T$_{10}$ has 10 equivalent silicons resonating at -69.6 ppm; T$_{12}$ has two inequivalent silicon environments resonating at -69.1 ppm and at -72.0 ppm in a ratio of 1:2.
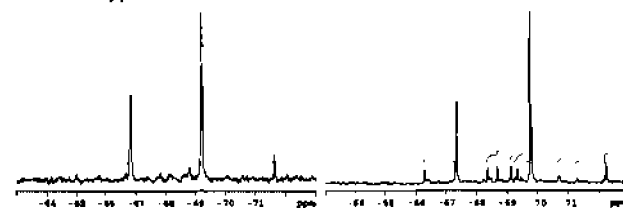

Figure 4. ^{29}Si NMR spectra of fluoroPOSS plus NEt$_3$ in C$_6$F$_6$ after several weeks; fluoropropyl is on the right (131 days) and fluorohexyl is on the left (42 days).

Comparing figures four and three demonstrates that the thermodynamic ratio of cages is very similar for fluoropropyl and fluorohexylPOSS. In

addition, the higher oligomers can be seen "growing in" when the reaction is allowed to proceed for extended periods of time.
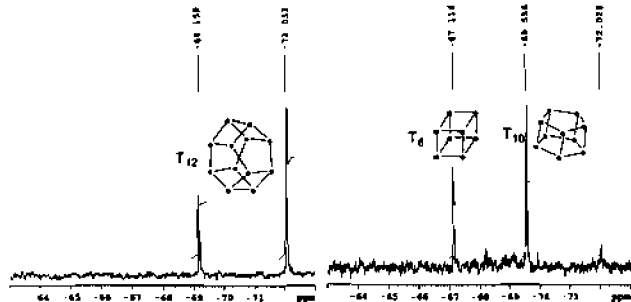

Figure 5. ^{29}Si NMR spectra of fluoropropyl$_{12}$T$_{12}$ in C$_6$F$_6$ before NEt$_3$ addition (on left) and 4 days later after addition of base (on right).

The data in figure 5 shows the definitive experiment proving that for fluoropropylPOSS. the thermodynamically favored products in C$_6$F$_6$ are T$_8$, T$_{10}$ and T$_{12}$ in a ratio of about 40:50:10. In this case, the starting POSS compound was pure T$_{12}$ and after a few days equilibrating with NEt$_3$ catalyst in C$_6$F$_6$, most of the T$_{12}$ was replaced with predominately T$_8$ and T$_{10}$.

The choice of solvent can also affect the equilibration. It is much slower in THF, and barely takes place in AK225G, CClFH(CF$_2$)CF$_2$Cl. It is possible that the acidic proton in the AK225G solvent ties up the NEt$_3$ catalyst to slow the reaction. In mixed C$_6$F$_6$ / Freon113 solvent, as the fluoropropylT$_x$ equilibrates, the small amounts of T$_{12}$ produced are barely detectable by ^{29}Si nmr spectroscopy because it nearly quantitatively precipitates from solution, milking the T$_{12}$ isomer from the others.
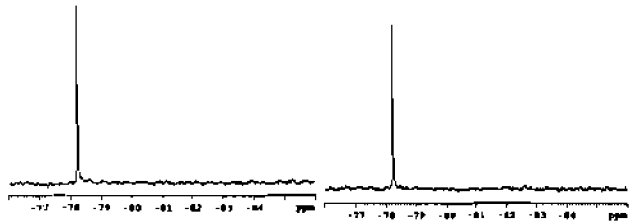

Figure 6. ^{29}Si NMR spectra of styrenyl$_8$T$_8$ in CDCl$_3$ before base addition (on left) and 118 days after adding NEt$_3$ (on right).

Under similar conditions to that tried with the fluoroalkylPOSS, no equilibration occurred to cyclohexyl$_x$T$_n$, cyclohexyl$_8$T$_8$, vinyl$_8$T$_8$ or styrenyl$_8$T$_8$, demonstrating that there is something in the nature of the fluoroalkyl groups that induces kinetic lability to these cages in the presence of soft base. Both electron-donating alkyl and electron-withdrawing alkenyl groups seem to be immune to this equilibration with triethylamine. However, stronger bases should promote the reaction.[4]

Conclusions

It is apparent that although the T$_8$ structure is the most common type of POSS, it is likely not the most thermodynamically stable motif, both theory and experiment show this to be the case. Under conditions where a soluble POSS cage is exposed to a mild "soft" base such as NEt$_3$, T$_8$ cages with very electron-withdrawing fluoroalkyl groups (-CH$_2$CH$_2$(CF$_2$)$_n$CF$_3$), slowly convert to mixtures favoring larger cages. This reaction does not affect POSS cages with electron donating alkyl groups or those with electron-withdrawing alkenyl groups. It is presumed that the fluoroalkyl group increases the lability of the polarizable Si-O bond opening a kinetic pathway that allows the isomerization to take place. Clearly, when POSS with electron-withdrawing groups is incorporated into polymers containing basic sites, one must be aware that under certain conditions, it might be possible for the cages to rearrange into an alternate structure. For tethered POSS copolymers this pathway could lead to polymer chain crosslinking.

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